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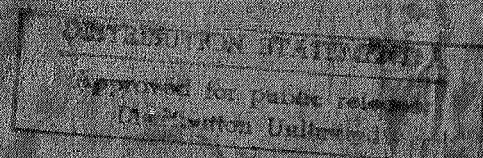
EVAPORATIVE SEGREGATION IN
80% Ni-20% Cr AND
60% Fe-40% Ni ALLOYS

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GRUMMAN AEROSPACE CORPORATION
BETHPAGE NEW YORK

EVAPORATIVE SEGREGATION IN 80% Ni-20% Cr
AND 60% Fe-40% Ni ALLOYS

by

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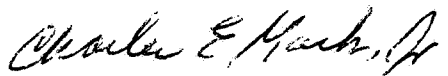
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ABSTRACT

The phenomenon of evaporative segregation in binary alloys has been investigated through a study of some experimental evaporation data relating to the Ni-Cr and Ni-Fe systems. In normal evaporation it is assumed that a) the evaporating alloy is always homogeneous, b) the vapor is instantly removed, and c) the alloy follows Raoult's law. The solutions of the evaporation equations for the two most important cases are presented and experimental data are analyzed with these equations. The difference between observed and calculated values of evaporation constants lies within one order of magnitude. This is surprising because of the major assumptions stated above. Experimental results have shown that the evaporation time t and final solute concentration m are logarithmically related, further supporting our evaporation equations. It is further shown that neglecting the nonlogarithmic term in these evaporation equations may introduce considerable errors in the analysis.

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DISCUSSION

The phenomenon of evaporative segregation in binary alloys has been quantitatively treated by Li (Refs. 1,2). By evaporative segregation, we mean solute enrichment or depletion in the evaporating alloy as a result of surface evaporation.

The formalism of evaporative segregation in alloys works surprisingly well for the several systems so far studied, notwithstanding the several major assumptions involved. In the present memorandum, we shall study only some experimental evaporation data relating to the Ni-Cr and Ni-Fe systems, as reported by N. D. Obradovic et al. (Ref. 3). Specifically, we shall compute the degree and rate of solute enrichment or depletion in the evaporating source at different temperatures and evaporation times.

In the treatment of the simple "normal" evaporation, it is assumed that a) the evaporating alloy is always homogeneous, b) the vapor is instantly removed, and c) the alloy follows Raoult's law. Such conditions exist or are nearly approached in an induction melt in vacuum or liquid in space. The solutions of the relevant differential equation for the following two important cases are (Ref. 2):

Case I: The solute is much more evaporative than solvent, i.e., $U \gg V$. Then the time to reach a final concentration m is

$$t_1 = G_1 \left[\ln \frac{(1 - m_o)m}{m_o(1 - m)} + \frac{m - m_o}{(1 - m_o)(1 - m)} \right] \quad (1)$$

where

$$G_1 = - N_0(1 - m_0)/AU \text{ (sec)}$$

$$U = \text{evaporation rate of the solute in mol/cm}^2/\text{sec}$$

$$V = \text{evaporation rate of the solvent in mol/cm}^2/\text{sec}$$

$$m_0 = \text{initial molar fraction of solute}$$

$$m = \text{final molar fraction of solute after time } t_1 \text{ (in sec)}$$

$$N_0 = \text{total initial number of moles of both solvent and solute}$$

$$A = \text{evaporating area in cm}^2$$

For nearly equal m and m_0 (i.e., $m \simeq m_0$), or for small m and m_0 (i.e., $m \simeq m_0 \simeq 0$), Eq. (1) reduces to the following logarithmic expression:

$$t_1 = G_1 \ln \left[\frac{(1 - m_0)m}{m_0(1 - m)} \right] \quad (1a)$$

Case II: The solvent is much more evaporative than solute, i.e., $V \gg U$, then,

$$t_2 = G_2 \left[\ln \frac{(1 - m_0)m}{(1 - m)m_0} + \frac{m - m_0}{mm_0} \right] \quad (2)$$

where $G_2 = m_0 N_0 / AV$. Again, for nearly equal m and m_0 (i.e., $m \simeq m_0$), Eq. (2) reduces to a logarithmic expression very similar to (1a):

$$t_2 = G_2 \ln \left[\frac{(1 - m_0)m}{m_0(1 - m)} \right] \quad (2a)$$

G 's are the time constants of evaporation. For the case when $U \gg V$, solute depletion takes place, i.e., $m < m_0$ and, therefore, the logarithmic term in the parentheses is negative (the second term in the parentheses is often negligible by comparison with the logarithmic term). Since the evaporation time, t , must be positive, G_1 is negative, G_2 is always positive.

The evaporation rate in $\text{mol/cm}^2/\text{sec}$ for solute and solvent is given by (Ref. 4)

$$U = K \left(10^{A_u - B_u/T} \right) / \sqrt{M_u T} \quad (3)$$

$$V = K \left(10^{A_v - B_v/T} \right) / \sqrt{M_v T} \quad (4)$$

where

$K = 5.833 \times 10^{-5}$, a constant for metals

M_u, M_v = molecular weights of solute and solvent, respectively

T = evaporating temperature in $^{\circ}\text{K}$

A_u, B_u = evaporating constants for the solute

A_v, B_v = evaporating constants for the solvent.

Obradovic et al. (Ref. 3) give the final solute concentrations for Ni-Fe and Ni-Cr alloys after various evaporating times at 1600°C under various ambient pressures, as shown in Tables 1 and 2. These data have been analyzed by means of Eqs. (1) and (2), above. The solute and solvent evaporating constants, A_u , B_u , A_v , and B_v , are obtained from Ref. 4.

Table 1

CALCULATED AND OBSERVED VALUES OF G_2 's FOR Fe-Ni

60% Fe-40% Ni Alloy

Log $x = 1.7915$ at $t = 0$, G_2 calc. ($\times 10^{-4}$) = 0.4369 sec

No.	Ambient Pressure ($\times 10^3$) Torr	Log x ($x = \text{wt } \% \text{ Fe}$) after 1800 secs	G_2 ($\times 10^{-4}$)		G_2 (logarithmic term) $\frac{G_2(\text{two terms})}{G_2(\text{calculated})}$	G_2 (two terms) $\frac{G_2(\text{two terms})}{G_2(\text{calculated})}$
			Two Terms	Logarithmic Term Only		
1	1	1.7787	1.4302	2.3923	1.67	3.27
2	5	1.7877	4.8355	8.0034	1.65	11.06
3	30	1.7812	1.7763	2.9627	1.67	4.06
4	50	1.7775	1.3034	2.1835	1.67	2.98
5	100	1.7710	0.8934	1.5080	1.68	2.04
6	200	1.7805	1.6942	2.8274	1.66	3.87
7	500	1.7862	3.4573	5.7324	1.67	7.91

Table 2

CALCULATED AND OBSERVED VALUES OF G_1 's FOR Ni-Cr ALLOY

80% Ni-20% Cr Alloy

Log x = 1.2920 at t = 0, $-G_1$ calc. ($\times 10^{-4}$) = 0.1710 sec

No.	Ambient Pressure ($\times 10^3$) Torr	Log x (x = wt % Cr) after 1800 secs	$-G_1$ ($\times 10^{-4}$)		G_1 (logarithmic term) $\frac{G_1(\text{two terms})}{G_1(\text{calculated})}$	G_1 (two terms) $\frac{G_1(\text{two terms})}{G_1(\text{calculated})}$
			Observed, secs	Logarithmic Term Only		
1	1	1.2600	1.5690	1.9815	1.26	9.17
2	5	1.2746	2.8730	3.6439	1.26	16.80
3	30	1.2663	1.9493	2.4663	1.26	11.39
4	50	1.2793	3.9210	4.9800	1.27	22.92
5	100	1.2773	3.3902	4.3033	1.26	19.82
6	200	1.2856	7.8135	9.9428	1.27	45.69
7	500	1.2826	5.3112	6.7525	1.27	31.05

Relevant data for computation of the G 's are given below:

a) 60% Fe-40% Ni alloy:

$$U_{\text{Ni}} = 6.386 \times 10^{-6} \text{ mol/cm}^2/\text{sec}; N_o = 0.7478 \text{ mol}; T = 1600^\circ\text{C};$$

$$V_{\text{Fe}} = 1.081 \times 10^{-5} \text{ mol/cm}^2/\text{sec}; A = 10.0 \text{ cm}^2; \text{Case II: } U \ll V.$$

b) 80% Ni-20% Cr alloy:

$$U_{\text{Cr}} = 3.479 \times 10^{-5} \text{ mol/cm}^2/\text{sec}; N_o = 0.7582 \text{ mol}; T = 1600^\circ\text{C};$$

$$V_{\text{Ni}} = 6.386 \times 10^{-6} \text{ mol/cm}^2/\text{sec}; A = 10.0 \text{ cm}^2; \text{Case I: } U \gg V.$$

It can be seen from Table 1 that for the Fe-Ni alloy, the values of G_2 's are constant within one order of magnitude. The difference between observed and calculated values of G_2 is also within one order of magnitude. This is very surprising considering the fact that elemental evaporation rates generally differ by many orders of magnitude. Also, the above analysis is based on the assumptions of a) the evaporating alloy is always homogeneous; b) ideal solution behavior (and the solutions here are highly concentrated!); c) the vapor is instantly removed. The experimental data of Obradovic et al. (Ref. 3) on the Fe-Ni system shows no systematic dependence of evaporation kinetics on pressure as one would expect, and suggests large experimental errors, errors in measurements, or both.

Table 2 also shows the calculated and observed values of G_1 's for the Ni-Cr alloy. Here, also, the values of G_1 's are almost constant, and the differences between the observed and calculated values of G_1 's are small. The data on the Ni-Cr system show some positive correlation between ambient pressure and the weight percent of chromium in the melt after 30 minutes.

The values of computed G 's are constant within one order of magnitude. In particular, for the Fe-Ni system, at ambient pressures of 1, 30, 50, 200 ($\times 10^3$) torr, these same values are accurate to within 25 percent. Therefore, in some cases it is desirable to know these values to within 20 percent of their real values.

In Tables 1 and 2 the time constants G 's have been calculated in two ways. First, G 's were calculated by using only the logarithmic term. Next, the complete equation (1) or (2) involving both the logarithmic and nonlogarithmic terms was used. It is interesting to note that the ratio of G 's calculated in two cases is constant and has an average value of 1.67 ± 0.01 for Fe-Ni alloy and 1.26 ± 0.005 for the Ni-Cr alloy. Mathematically, this means that for the case $U \gg V$ (in Ni-Cr alloy)

$$\frac{\ln \left[\frac{(1 - m_o)m}{m_o(1 - m)} \right] + \frac{m - m_o}{(1 - m_o)(1 - m)}}{\ln \left[\frac{(1 - m_o)m}{m_o(1 - m)} \right]} = 1.26 , \quad (5)$$

or

$$\frac{\frac{m - m_o}{(1 - m_o)(1 - m)}}{\ln \left[\frac{(1 - m_o)m}{m_o(1 - m)} \right]} = 0.26 , \quad (6)$$

and for the case $V \gg U$, i.e., in Fe-Ni alloy

$$\frac{\frac{m - m_o}{m_o m}}{\ln \left[\frac{(1 - m_o)m}{m_o(1 - m)} \right]} = 0.67 . \quad (7)$$

Experimental results have shown that the evaporation time t and the final solute concentration m are logarithmically related (Refs. 3,5), supporting our Eqs. (1) and (2). However, these same equations indicate that such relations are true only for vastly different solvent and solute evaporating rates, and, in addition, for small initial and final concentrations, m_o and m . These same equations also allow one to compute, e.g., the effective evaporating area, A , the solute or solvent evaporating rates U or V , or the evaporating temperature T . Further, neglecting the nonlogarithmic second terms in Eqs. (1) and (2) may introduce errors in T , A , U , or V by 26 percent in the 80% Ni-20% Cr case and 67 percent in the 60% Fe-40% Ni case.

The equations of normal evaporation can be made more realistic by introducing the concept of solvent-solute interaction. If one considers only first-order correction, then it can be shown that the ideal evaporation rates of solutes and solvents will be changed by a new factor related to the activity coefficient of the element in question. In other words,

$$\begin{aligned} U' &= \gamma_u U \\ V' &= \gamma_v V , \end{aligned} \quad (8)$$

where γ_u , γ_v are activity coefficients of solute and solvent, respectively, assumed constant in the vicinity of m_o ; and U' , V' are effective evaporating rates of solutes and solvents. Using the activity data of Fe-Ni alloy (Ref. 6) at 1600°C, we have recalculated the values of G_2 . Now

$$G'_2 = \frac{m_o n_o}{AV'}$$

where

(9)

$$V' = \gamma_v V$$

$$\gamma_v = \gamma_{Fe} = 0.977 \quad \text{for} \quad 60 \text{ mol } \% \text{ Fe alloy.}$$

$$G'_2 \text{ (cal)} = 0.4471 \times 10^{+4} \text{ sec.}$$

On applying similar first-order correction for Ni-Cr system (Ref. 7), the revised value of G_1 becomes,

$$G'_1 \text{ (cal)} = 0.2138 \times 10^{+4} \text{ sec.}$$

These corrections, while not very large, do make a little better agreement between calculated and experimentally observed G values.

In conclusion, the simple normal evaporation approach seems to give fairly accurate and useful predictions, even for the highly concentrated Ni-Cr and Fe-Ni alloys.

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